

# **New Ion-Molecule Reactions for Titan's Ionosphere**

**Murray J McEwan<sup>1</sup>, Graham B. I. Scott,**

Department of Chemistry,  
University of Canterbury,  
Christchurch, New Zealand

and

**Vincent G. Anicich**

Jet Propulsion Laboratory,  
California Institute of Technology,  
4800 Oak Grove Dr,  
Pasadena, CA 91109, USA  
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<sup>1</sup> NRC-NASA Research Associate at JPL 1993/94

## **Abstract**

Twenty-four new ion-molecule reactions are presented for inclusion in the modeling of the ionosphere of Saturn's satellite Titan. Sixteen reactions were re-examined to reduce uncertainties in the previous literature results. The ions selected for this study were derived either from nitrogen, appropriate hydrocarbons or nitriles. The reactant neutrals were selected on the basis of their known presence in Titan's atmosphere. The reaction products are consistent with the expected increase in ion size through ion-molecule reaction processing. Data is also presented for the reactions of twenty-three ions with molecular nitrogen. Almost all of these ions are non reactive with  $N_2$ .

## Introduction

In October of 1997 it is anticipated that a Titan IVB rocket will launch a payload from the Earth and project it on a circuitous course that will eventually take it into orbit around the planet Saturn.<sup>1</sup> The payload will be the Cassini space craft with a special probe named after the astronomer Huygens. During orbit around Saturn the spacecraft will use the gravity of the Saturnian satellite Titan to alter its trajectory, thereby facilitating a comprehensive exploration of Saturn and its moons. This procedure requires the spacecraft to fly through the ionosphere of Titan.

Titan has been explored previously by the pair of Voyager spacecraft using optical spectroscopy<sup>2</sup> and also radio occultations.<sup>3</sup> Titan has also been studied using Earth-based astronomical telescopes. These studies show that Titan has the most extensive atmosphere of any planetary satellite in our solar system. While Titan is much less massive than Earth it has a slightly larger atmospheric pressure at its surface. Compared with Earth, the atmosphere of Titan has a greater depth due to its smaller mass. Titan's atmosphere consists mainly of nitrogen gas (94%) with the remaining 6% of the atmosphere consisting of the hydrocarbon gases: methane, acetylene, ethylene and ethane.<sup>4</sup> It is also known that HCN, CH<sub>3</sub>CN, HC<sub>3</sub>N, and C<sub>2</sub>N<sub>2</sub> are present in much lower abundances.<sup>4</sup>

A quadrupole mass spectrometer on the Cassini spacecraft will sample the neutrals and ions present in Titan's ionosphere.<sup>5</sup> It is therefore necessary to gain an understanding of the ion chemistry that might occur in such an environment. Many of the pertinent reactions have previously been characterised.<sup>6</sup> The twenty-four new reactions and twenty-one non-reactions reported here will add greatly to the modeling of Titan's atmosphere. This information will help in planning the exploration strategy for Titan's ionosphere and also in the interpretation of the mass spectra obtained.

## Experimental

The Jet Propulsion Laboratory ion cyclotron resonance mass spectrometer (ICR) has been described in detail previously<sup>7,8</sup> and so only a brief description is given here. The instrument is based on a 12 inch electromagnet which typically operates at a constant magnetic field of 1.5T and stores ions in an

ICR cell that can either be used as a trap-drift cell or a simple drift cell.<sup>9</sup> Separate trapping plates are located in both the source and resonance regions. The cyclotron frequency of the ions is utilized to monitor ion concentrations within the cell. The ions are detected at their cyclotron frequencies by a capacitance bridge detector.<sup>10</sup>

The low pressure bimolecular reaction rate coefficients are determined by analyzing the variation of reactant ion signal intensity with time in the trap-mode operation of the ICR spectrometer. Detailed descriptions of the measurement and data analysis technique have been published previously.<sup>11</sup> Double resonance experiments<sup>13</sup> are conducted to determine reaction pathways and to measure the branching ratios. All gas pressures are measured by a Bayard-Alpert ion gauge which has been calibrated against a capacitance manometer (MKS Baratron with a one Torr head). The experiments were conducted at 298 K. The second-order reaction rate constants have an estimated error bar of \*15%, due principally to the inaccuracy of the pressure determination and control. The third-order reaction rate constants have an expected error bar of  $\pm 30\%$ . Product branching ratios have an estimated error of  $\pm 5\%$ . The reactant ions are generated by near threshold electron impact ionization, dissociative ionization, or through ion-molecule chemistry.

An ICR tandem mass spectrometer was also used in these studies. This has an ICR-Dempster-ICR configuration. This instrument was built at UCSB and has been described previously.<sup>14</sup> It has been relocated to JPL. The instrument is based on a 12 inch electromagnet which is typically operated at a constant Dempster field of 3 kV. The ion source is a two section ICR cell operating in the drift-mode. Similarly the ion detector is another two section ICR cell operating in the drift-mode. All three parts of the instrument are within the same 12 inch electromagnetic field. The design is an adaptation of that used by Smith and Futrell.<sup>15</sup> Instead of the standard Dempster source, an ICR cell was used as the ion source. Ions generated in this cell are accelerated to typically 3000 volts and bent through 180 degrees. The second ICR cell is located 4.74 cm from the first and the desired ions are guided into this second ICR by adjusting the magnetic field. The ions are decelerated and introduced into the second ICR through a 0.5 mm thick Wein filter which is 3.8 mm long. This design only allows ions with less than 0.3 eV of transitional

energy to enter the detection cell. A Wronka bridge detection circuit<sup>10</sup> is used to measure the ion abundances within the detection cell.

Higher pressure measurements (0.35 Torr of He) were made using the Selected Ion Flow Drift Tube (SIFDT) at Canterbury University.<sup>16</sup> In the SIFDT technique, rate coefficients are usually determined from the rate of removal of the reactant ion under pseudo-first order conditions. Reactant ions are generated in an electron impact source and mass-filtered using a quadrupole mass spectrometer. The mass selected ion beam is introduced into a flowing stream of helium gas through a venturi-orifice. The flow tube is 6.03 cm in diameter and 1.085 m long. At 0.35 Torr pressure of helium, the gas velocity is about 12000 cm S<sup>-1</sup>. The ions are in a swarm and travel through the tube 1.5 times faster on the tube axis, than the carrier gas. At the detector, the ions are sampled through a small orifice into a differentially pumped quadrupole mass spectrometer. Ions are counted using a channeltron ion multiplier and pulse height discriminator. Typical count rates are between 1,000 and 20,000 cps.

Reagent species (except for HC<sub>3</sub>N) were obtained from commercial sources and further purified by freeze-pump-thaw cycles. All measurements were made at room temperature  $298 \pm 5$  K. HC<sub>3</sub>N was prepared by the action of methyl propiolate and NH<sub>3</sub> followed by dehydration with P<sub>2</sub>O<sub>5</sub> as described previously.<sup>12,17</sup>

## Results

The results obtained in this work have been summarized for the N<sup>+</sup> and N<sub>2</sub><sup>+</sup> reactions in Table 1 and for the hydrocarbon ions and the other ions in Table 2. Both the neutral products and the ion structures in these Tables are deduced from thermochemical considerations. The reported products are consistent with the lowest energy states. All of the reactions reported are exothermic at 300 K.

The branching ratios for a number of reactions were found using the tandem mass spectrometer to avoid problems arising from mass overlap of product ions and reactant ions (e.g. N<sub>2</sub><sup>+</sup> and C<sub>2</sub>H<sub>4</sub><sup>+</sup>) and ambiguities of mass overlap between product ions themselves (e.g. CN<sup>+</sup> and C<sub>2</sub>H<sub>2</sub><sup>+</sup>). In some of these cases it was also necessary to use deuterium labelled hydrocarbons and/or isotopically labelled <sup>15</sup>N nitrogen. When identifying the products from the N<sup>+</sup> and N<sub>2</sub><sup>+</sup> reactions with hydrocarbon ions (Table 1)

the use of the tandem mass spectrometer ensured that only  $N^+$  or  $N_2^+$  was present before the addition of the reactant neutral.  $C_2D_4$  as well as  $C_2H_4$  was used to identify the ion products of  $N^+$  and  $N_2^+$  with  $C_2H_4$ . Similarly,  $C_2D_6$  as well as  $C_2H_6$  was used to identify the ion products of  $N^+$  and  $N_2^+$  with  $C_2H_6$ . In addition both  $^{14}N_2^+$  and  $^{15}N_2^+$  were used to interpret the ion products of  $N_2^+$  with  $CH_4$ ,  $C_2H_2$  and  $C_2H_4$ . The ion products of these reactions were deconvoluted from the range of possibilities by using these isotopic substitutions.

The tandem mass spectrometer was also used to determine the product ions of the reactions of  $C_3H_5^+$  with  $C_2H_2$ ,  $HCN$ ,  $HC_3N$  and  $CH_2CHCN$ . The kinetic information reported other than that mentioned above was obtained from the conventional ICR spectrometer. Branching ratios in this instrument were obtained using the drift mode and cyclotron resonance ejection on the parent ion. Reaction rate coefficients were obtained using the conventional ICR spectrometer in the trapped mode and following the decay of the parent ion with time.

Twenty-one ions were found to be unreactive with molecular nitrogen using the SIFT experiment with a helium bath gas at 0.35 Torr.  $CH_3^+$ ,  $C_2H_2^+$ ,  $C_2H_3^+$ ,  $C_2H_4^+$ ,  $C_2H_5^+$ ,  $C_3^+$ ,  $C_3H^+$ ,  $C_3H_2^+$ ,  $l-C_3H_3^+$ ,  $c-C_3H_3^+$ ,  $C_3H_5^+$ ,  $C_4H_3^+$ ,  $c-C_6C_6^+$ ,  $HCN^+$ ,  $HCNH^+$ ,  $HC_3N^+$ ,  $HC_3NH^+$ ,  $H_3O^+$ ,  $O^+$ , and  $CO_2^+$  all had reaction rate coefficients that were less than  $5 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ .  $CN^+$  had a reaction rate coefficient that was less than  $6 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ .

The reaction of  $CO^+$  with  $N_2$  formed an adduct with an effective pseudo second order reaction rate coefficient of  $5.3 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ . This rate coefficient is consistent with a third order reaction rate coefficient of  $4.7 \times 10^{-29} \text{ cm}^6 \text{ s}^{-1}$  and compares favourably with an earlier value of  $2.1 \times 10^{-29} \text{ cm}^6 \text{ s}^{-1}$  in a helium buffer.<sup>41</sup> We assume that the adduct product is produced solely by a third order reaction.

We also observed the reaction of  $H_3^+$  with  $N_2$  and measured its reaction rate coefficient as  $1.63 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  when  $H_3^+$  was formed in an endothermic reaction of  $KrH^+ + H_2$  as described elsewhere.<sup>42</sup>

## Discussion

### $\text{N}^+$ Reactions

The data on the reactions of  $\text{N}^+$  with  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_6$ ,  $\text{CH}_3\text{CN}$ , and  $\text{CH}_2\text{CHCN}$  has not been published previously. The data on the reactions of  $\text{N}^+$  with  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ ,  $\text{HCN}$ , and  $\text{HC}_3\text{N}$  were repeated in an attempt to validate the results found in the literature.<sup>6</sup> Generally these required the use of tandem mass spectrometry to accurately measure the branching ratios with reduced ambiguity of mass overlaps. The present results for the reaction  $\text{N}^+/\text{CH}_4$  agree very closely with the published evaluated value.<sup>6</sup> The values of the branching ratio for  $\text{N}^+/\text{C}_2\text{H}_4$  presented here agree with those of Smith and Adams<sup>22</sup> and not with those of Rakshit,<sup>43</sup> both published in 1980 and using SIFT instruments. Our tandem results of the reaction of  $\text{N}^+/\text{HCN}$  show a 35% channel forming  $\text{CH}^+ + \text{N}_2$  which was not reported by Clary *et al* in 1990.<sup>23</sup> The results of  $\text{N}^+/\text{HC}_3\text{N}$  differ slightly from the 50:50 results of Knight *et al* in 1985.<sup>24</sup>

In all cases the charge transfer channels are major channels except in the two reactions of  $\text{N}^+/\text{CH}_4$  and  $\text{N}^+/\text{C}_2\text{H}_6$ . Also in all cases there is significant evidence of molecular rearrangement occurring with the  $\text{N}^+$  ion being incorporated into the hydrocarbon or nitrile.

### $\text{N}_2^+$ reactions

The data on the reactions of  $\text{N}_2^+$  with  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{HCN}$ , and  $\text{CH}_2\text{CHCN}$  represent first published results. The data on the reactions of  $\text{N}_2^+$  with  $\text{CH}_4$ ,  $\text{C}_2\text{H}_2$ , and  $\text{HC}_3\text{N}$  were repeated in an attempt to validate results found in the literature.<sup>6,44</sup>

In the reaction of  $\text{N}_2^+/\text{CH}_4$ , we report for the first time the H atom abstraction channel forming  $\text{N}_2\text{H}^+ + \text{CH}_3$ . This had been noted in the reaction of  $\text{N}_2^+/\text{CD}_4$  in two early studies.<sup>45, 46</sup> The ratio of the channels,  $\text{CH}_2^+$  and  $\text{CH}_3^+$ , is broadly consistent with previously reported studies.<sup>20,25,26</sup>

The reaction of  $\text{N}_2^+/\text{C}_2\text{H}_2$ , had been studied using photionization mass spectrometry (PIMS)<sup>27</sup> and the charge transfer channel was noted in this work. Using the tandem mass spectrometer we were able to identify two other active channels with the H atom abstraction channel predominating. The reaction rate coefficient reported here is consistent with the PIMS study.

In the case of the reaction of  $\text{N}_2^+/\text{HC}_3\text{N}$ , we were also able to identify the presence of H atom abstraction which was not reported in earlier studies.<sup>24,29</sup>

In all of the measured  $\text{N}_2^+$  reactions, charge transfer with the loss of a hydrogen atom is the major reaction channel except in those reactions which have higher bond energies such as the triple bond molecules  $\text{C}_2\text{H}_2$ ,  $\text{HCN}$ , and  $\text{HC}_3\text{N}$ . With these reactants charge transfer from  $\text{N}_2^+$  is a common channel.

## Reactions with $\text{N}_2$

It was noted that both  $\text{C}_2\text{H}_2^+$  and  $\text{C}_2\text{H}_5^+$  ions were not measurably reactive with molecular nitrogen. This observation is consistent with the pool of information<sup>6,44</sup> that is available for ion reactions with molecular nitrogen. Primarily if an ion reacts with molecular nitrogen it does so by either charge transfer or proton transfer. Since the ionization potential of molecular nitrogen is 15.58 eV,<sup>47</sup> there are very few ions that have enough energy to ionize it, viz:  $\text{He}^+$ ,  $\text{He}_2^+$ ,  $\text{F}^+$ ,  $\text{Ne}^+$ , and  $\text{Ar}^+$ . Further, the proton affinity of molecular nitrogen is so low, 118.2 kcal/mol<sup>47</sup> that few ions that will proton transfer to it. Only  $\text{H}_2^+$ ,  $\text{H}_3^+$ ,  $\text{NH}^+$ ,  $\text{OH}^+$ ,  $\text{HeH}^+$ ,  $\text{ArH}^+$ ,  $\text{KrH}^+$ ,  $\text{XeH}^+$ , and  $\text{O}_2\text{H}^+$  proton transfer to molecular nitrogen. All other ions that have been studied in reactions with  $\text{N}_2$  do not react with it.<sup>6,44</sup>

Of the non-reactions measured using the SIFT experiment,  $\text{C}_2\text{H}_2^+$ ,  $\text{C}_2\text{H}_3^+$ ,  $\text{C}_2\text{H}_4^+$ ,  $\text{C}_2\text{H}_5^+$ ,  $\text{C}_3^+$ ,  $\text{C}_3\text{H}_2^+$ ,  $\text{l-C}_3\text{H}_3^+$ ,  $\text{c-C}_3\text{H}_3^+$ ,  $\text{C}_3\text{H}_5^+$ ,  $\text{C}_4\text{H}_3^+$ ,  $\text{c-C}_6\text{H}_6^+$ ,  $\text{HCNH}^+$ ,  $\text{HC}_3\text{N}^+$ ,  $\text{H}_2\text{C}_3\text{N}^+$ ,  $\text{H}_3\text{O}^+$ , and  $\text{CO}_2^+$  are reported here for the first time.  $\text{CH}_3^+$ ,<sup>4, 8, 49</sup>  $\text{C}_3\text{H}^+$ ,<sup>50</sup>  $\text{HCN}^+$ ,<sup>28</sup>  $\text{CO}^+$ ,<sup>41</sup>  $\text{O}_2^+$ ,<sup>51,52</sup> and  $\text{CN}^+$ <sup>53, 54</sup> have been reported previously as being non-reactive. The results that we present are consistent with these other reported findings for these six ions.

The measured reaction rate coefficient of  $\text{H}_3^+$  with  $\text{N}_2$  was within the experimental error of the evaluated reaction rate coefficient for this reaction of  $1.86 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ .

## Reactions with **Hydrocarbon** Neutrals

The reactions of  $\text{C}_3\text{H}_5^+$  with  $\text{CH}_4$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{D}_2$  and  $\text{C}_2\text{H}_6$  are reported here for the first time.  $\text{C}_3\text{H}_5^+$  is unreactive with the saturated species  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$ . It is however reactive with the less saturated species  $\text{C}_2\text{H}_2$  and  $\text{C}_2\text{H}_4$  forming a  $\text{C}_5$  hydrocarbon ion with the loss of  $\text{H}_2$ . At higher pressures



an adduct is observed for  $C_2H_4$ .<sup>30</sup> It was not determined whether adduct formation was via a two-body or three-body process.

The reactions of  $C_2H_3^+$  and  $C_2H_4^+$  with  $C_2H_4$  have been measured many times previously. Our results are within experimental error of the 1993 evaluations.<sup>6</sup>

The  $CHCCNH^+$  and  $HC_5N^+$  reactions with  $C_2H_4$  are reported on for the first time. These two ions were prepared by ensuing reactions after initial electron impact on cyanoacetylene,  $HC_3N$ . The product ions of the reactions with  $C_2H_4$  are expected to be mixtures of acyclic and cyclic structures.

The reaction of the cyanogen ion with acetylene has been studied before.<sup>31</sup> In our studies we found two condensation channels in addition to the charge transfer reaction previously reported. Our measured reaction rate coefficient is only about a third of that reported previously. The reverse reaction  $C_2H_2^+ + C_2N_2$  was also studied and found not to react. We place an upper limit on the reaction rate coefficient for this reaction as  $k < 2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ .

We also found no evidence of a reaction between  $HCNH^+$  and  $C_2H_6$  in the ICR instrument. Since, HCN has the higher proton affinity this result is expected.

The reaction between the propene ion  $C_3H_6^+$  and propene has been studied previously.<sup>35</sup> Our present result has branching ratios that are similar to those from the previous study, but our measured reaction rate coefficient is twice that reported in the previous study.

### Reactions with HCN

The reactions of  $C_2H_6^+$ ,  $C_3H_5^+$ ,  $C_3H_6^+$ ,  $c\text{-}C_3H_6^+$ , and  $NO^+$  with HCN are the first reported results on these systems.  $C_2H_6^+$  reacts primarily through a proton transfer mechanism, but there is a 5% condensation channel. The only product of the  $C_3H_5^+$  reaction is the adduct, indicating either a radiative association process or a very fast three body association channel. The products of the  $C_3H_6^+$  reaction were not identifiable, even though it had about the same reaction rate coefficient as the  $c\text{-}C_3H_6^+$  ion. A similar situation was observed in the reaction between  $CH_3^+$  and HCN and may be indicative of an association channel.<sup>55</sup>  $c\text{-}C_3H_6^+$  formed an ion corresponding to  $H_6C_4N^+$ , which may have the structure  $C_3H_5CNH^+$ . No reaction was observed to occur between  $NO^+$  and HCN.

The reaction between  $\text{C}_2\text{N}_2^+$  and HCN had been studied before.<sup>36,37,38</sup> There was a great difference between the reported reaction rate coefficients. We agree with the later measurement<sup>36</sup> in that the reaction proceeds at nearly the collision limit.

### Reactions with other Nitriles

The reaction of  $\text{C}_2\text{H}_4^+$  with  $\text{HC}_3\text{N}$  had been reported previously.<sup>39</sup> We report here the existence of a 15% channel leading to  $\text{H}_4\text{C}_5\text{N}^+ + \text{H}$ . This channel was not observed in the earlier work. The  $\text{C}_3\text{H}_5^+$  ion also reacts by proton transfer with  $\text{HC}_3\text{N}$ , however the rate is slow being only one tenth the efficiency of the analogous reaction of  $\text{C}_2\text{H}_4^+$ . This is an unexpected and surprising result as proton transfer from ac- $\text{C}_3\text{H}_5^+$  to  $\text{HC}_3\text{N}$  is  $-80 \text{ kJ mol}^{-1}$  more exothermic than is proton transfer from  $\text{C}_2\text{H}_4^+$ . A large component of c- $\text{C}_3\text{H}_5^+$  in the  $\text{C}_3\text{H}_5^+$  ion swarm may be responsible for this rate coefficient which is smaller than anticipated. Proton transfer from c- $\text{C}_3\text{H}_5^+$  to  $\text{HC}_3\text{N}$  is endothermic and this may indicate that the  $\text{C}_3\text{H}_5^+$  ion, which was generated by electron impact on  $\text{C}_2\text{H}_4$ , is a mixture of isomeric ions. This conjecture is also supported by the absence of proton transfer observed with HCN which is exothermic for ac- $\text{C}_3\text{H}_5^+$  but endothermic for c- $\text{C}_3\text{H}_5^+$ . The reaction of  $\text{C}_3\text{H}_5^+$  and  $\text{CH}_2\text{CHCN}$  is very similar to that observed with  $\text{HC}_3\text{N}$ , in that proton transfer occurs. There is also evidence of a three body association channel. No reaction of  $\text{C}_3\text{H}_5^+$  with  $\text{H}_2$  was found as has been reported elsewhere.<sup>40</sup>

## Conclusions

In the unique chemical mix of nitrogen and hydrocarbons that constitute the atmosphere of Titan, the chemical processing that occurs incorporates the most abundant species into a soup of interesting and exotic molecules. This chemical processing may be via heterogeneous reaction, or homogeneous gas phase reactions involving both ion and neutral chemistry. In the present work, the reactions we have studied show how some of the ion-neutral processing takes place. Of particular interest is how  $N_2$  is incorporated into hydrocarbon species. Although molecular nitrogen is unreactive to almost all ions we find that  $N^+$  and  $N_2^+$  ions do undergo a range of reactions with hydrocarbons in which some of the products are nitrile ions. These nitrile ions in turn react with further hydrocarbons forming larger nitriles.

The other series of ion-neutral reactions that are of special interest are the association reactions. We observed ion-neutral association occurring in several of the hydrocarbon ion nitrile reactions. Although the termolecular rate coefficients were not measured in the present study, we have measured several of these ion-association reactions in the past and find many are very fast with rate coefficients  $k_{\text{assoc}} - 10^{-23} \text{ cm}^6 \text{ s}^{-1}$  not being uncommon.<sup>8,56</sup> Ion association reactions that are this fast can compete with bimolecular channels at altitudes corresponding to the lower ionosphere of Titan.<sup>57</sup>

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**Table 1. Reactions of N<sup>+</sup> and N<sub>2</sub><sup>+</sup> ions with the listed neutral**

N+ Reactions	Products	Branching Ratio	Rate Coefficient cm <sup>3</sup> s <sup>-1</sup>	Previous Measurements
N <sup>+</sup> + CH <sub>4</sub>	CH <sub>3</sub> <sup>+</sup> + NH CH <sub>4</sub> <sup>+</sup> + N HCN <sup>+</sup> + H <sub>2</sub> + H HCNH <sup>+</sup> + H <sub>2</sub>	0.53 0.05 0.10 0.32		0.52 <sup>a</sup> 0.51 <sup>b</sup> 0.42 <sup>c</sup> 0.53 <sup>d</sup> (1.2X 10 <sup>-9</sup> ) <sup>e</sup> 0.06 0.03 0.06 0.04 0.09 0.06 0.14 0.10 0.33 0.40 0.38 0.32
N <sup>+</sup> + C <sub>2</sub> H <sub>2</sub>	C <sub>2</sub> H <sub>2</sub> <sup>+</sup> + N CNC <sup>+</sup> + H <sub>2</sub> CHNC <sup>+</sup> + H	0.70 0.15 0.15	1.50 X10 <sup>-9</sup>	
N <sup>+</sup> + C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>2</sub> <sup>+</sup> + NH <sub>2</sub> C <sub>2</sub> H <sub>3</sub> <sup>+</sup> + NH C <sub>2</sub> H <sub>4</sub> <sup>+</sup> + N HCN <sup>+</sup> + CH <sub>3</sub> HCNH <sup>+</sup> + CH <sub>2</sub> CHNC <sup>+</sup> + H <sub>2</sub> + H	0.10 0.25 0.35 0.10 0.15 0.05	1.30X10 <sup>-9</sup>	0.10 <sup>f</sup> (1.6 X 10 <sup>-9</sup> ) <sup>f</sup> 0.30 0.25 0.15 0.10 0.10 (CH <sub>2</sub> CN <sup>+</sup> )
N <sup>+</sup> + C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>5</sub> <sup>+</sup> + NH C <sub>2</sub> H <sub>4</sub> <sup>+</sup> + NH <sub>2</sub> C <sub>2</sub> H <sub>3</sub> <sup>+</sup> + NH <sub>3</sub> HCNH <sup>+</sup> + CH <sub>4</sub>	0.10 0.55 0.25 0.10		
N <sup>+</sup> + HCN	HCN <sup>+</sup> + N CH <sup>+</sup> + N <sub>2</sub>	0.65 0.35		log (3.7 x 10 <sup>-9</sup> ) <sup>g</sup>



N <sup>+</sup>	+ CH <sub>3</sub> CN	CH <sub>3</sub> CN <sup>+</sup>	+ N	0.50					
		CH <sub>2</sub> CN <sup>+</sup>	+ NH	0.30					
		[C <sub>2</sub> H <sub>2</sub> <sup>+</sup>	+ N <sub>2</sub> + H ]	0.20					
		[CN <sup>+</sup>	+ CH <sub>2</sub> NH ]						
N <sup>+</sup>	+ CH <sub>2</sub> CHCN	CH <sub>2</sub> CHCN <sup>+</sup>	+ N	0.35					
		H <sub>2</sub> C <sub>3</sub> N <sup>+</sup>	+ NH	0.15					
		[CHCN <sup>+</sup>	+ CH <sub>2</sub> N <sub>2</sub> 1	0.25					
		[LC-C3H3 <sup>+</sup>	+ N <sub>2</sub> ]						
		[CN <sup>+</sup>	+ CH <sub>3</sub> CN 1	0.25					
		[C <sub>2</sub> H <sub>2</sub> <sup>+</sup>	+ N <sub>2</sub> +CH ]						
N <sup>+</sup>	+ HC <sub>3</sub> N	C <sub>3</sub> H <sup>+</sup>	+ N <sub>2</sub>	0.25			0.50 <sup>h</sup> (4.2X 10 <sup>-9</sup> ) <sup>h</sup>		
		HCCCN <sup>+</sup>	+ N	0.75					0.50
N <sub>2</sub> <sup>+</sup> Reactions									
N <sub>2</sub> <sup>+</sup>	+ CH <sub>4</sub>	CH <sub>2</sub> <sup>+</sup>	+ N <sub>2</sub> + H <sub>2</sub>	0.05			0.08 <sup>i</sup> 0.07 <sup>j</sup> 0.11 <sup>c</sup> (1.14X 10 <sup>-9</sup> ) <sup>e</sup>		
		CH <sub>3</sub> <sup>+</sup>	+ N <sub>2</sub> + H	0.80					0.90
		N <sub>2</sub> H <sup>+</sup>	+ C H <sub>3</sub>	0.15					0.93
N <sub>2</sub> <sup>+</sup>	+ C <sub>2</sub> H <sub>2</sub>	C <sub>2</sub> H <sub>2</sub> <sup>+</sup>	+ N <sub>2</sub>	0.37	4.00x10 <sup>-10</sup>		1.0 <sup>k</sup> (4.3 x 10 <sup>-10</sup> ) <sup>k</sup>		
		HCN <sup>+</sup>	+ HCN	0.03					
		N <sub>2</sub> H <sup>+</sup>	+ C <sub>2</sub> H	0.60					
N <sub>2</sub> <sup>+</sup>	+ C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>3</sub> <sup>+</sup>	+ N <sub>2</sub> + H	0.50	1.30X10 <sup>-9</sup>				
		C <sub>2</sub> H <sub>2</sub> <sup>+</sup>	+ N <sub>2</sub> + H <sub>2</sub>	0.20					
		HNC <sup>+</sup>	+ HCN + H <sub>2</sub>	0.10					
		HCNH <sup>+</sup>	+ H C N + H	0.10					

$N_2^+$ + $C_2H_6$	$N_2H^+$	+ $C_2H_3$	0.10	-1.30X10 <sup>-9</sup>	
	$C_2H_6^+$	+ $N_2$			
	$C_2H_5^+$	+ $N_2$ + H			
	$C_2H_4^+$	+ $N_2$ + $H_2$			
	$C_2H_3^+$	+ $N_2$ + $H_2$ + H			
	$HCNH^+$	+ $CH_2NH_2$			
$N_2^+$ + HCN	$HCN^+$	+ $N_2$	1.00		$1.0^l (3.9 \times 10^{-10})^l$
$N_2^+$ + $CH_2CHCN$	$C_2H_3^+$	+ $N_2$ + CN	0.10		
	$C_2H_2^+$	+ $N_2$ + HCN	0.30		
	$H_2C_3N^+$	+ $N_2$ + H	0.35		
	$HC_3N^+$	+ $N_2$ + $H_2$	0.05		
	$N_2H^+$	+ $H_2C_3N$	0.20		
$N_2^+$ + $HC_3N$	$HC_3N^+$	+ $N_2$	0.70		$1.0^{h,m} (4.1 \times 10^{-9})^m$
	$N_2H^+$	+ $C_3N$	0.30		

Footnote for Table 1

- |              |             |              |             |
|--------------|-------------|--------------|-------------|
| <sup>a</sup> | See ref. 18 | <sup>b</sup> | See ref. 19 |
| <sup>c</sup> | See ref. 20 | <sup>d</sup> | See ref. 21 |
| <sup>e</sup> | See ref. 6  | <sup>f</sup> | See ref. 22 |
| <sup>g</sup> | See ref. 23 | <sup>h</sup> | See ref. 24 |
| <sup>i</sup> | See ref. 25 | <sup>j</sup> | See ref. 26 |
| <sup>k</sup> | See ref. 27 | <sup>l</sup> | See ref. 28 |
| <sup>m</sup> | See ref. 29 |              |             |

Table 2. Reactions of the given ion with the listed neutral reactant

Reactions with Hydrocarbons		Products	Branching Ratio	Rate Coefficient $\text{cm}^3 \text{s}^{-1}$	Previous Measurements
$\text{C}_3\text{H}_5^+$	+ $\text{CH}_4$	No Reaction		$<3.50 \times 10^{-11}$	
$\text{C}_3\text{H}_5^+$	+ $\text{C}_2\text{H}_2$	$\text{C}_5\text{H}_5^+$ + $\text{H}_2$	1.00	$3.80 \times 10^{-10}$	
$\text{C}_3\text{D}_5^+$	+ $\text{C}_2\text{D}_2$	$\text{C}_5\text{D}_5^+$ + $\text{D}_2$	1.00	$2.70 \times 10^{-10}$	
$\text{C}_3\text{H}_5^+$	+ $\text{C}_2\text{H}_4$	$\text{C}_5\text{H}_7^+$ + $\text{H}_2$ $\text{C}_5\text{H}_9^+$	0.70 0.30	$1.70 \times 10^{-10}$	$1.0^a (2.7 \times 10^{-10})^a$
$\text{C}_3\text{H}_5^+$	+ $\text{C}_2\text{H}_6$	No Reaction		$<5.00 \times 10^{-11}$	
$\text{C}_2\text{N}_2^+$	+ $\text{C}_2\text{H}_2$	$\text{C}_2\text{H}_2^+$ + $\text{C}_2\text{N}_2$ $\text{HC}_4\text{N}_2^+$ + $\text{H}$ $\text{C}_4\text{N}_2^+$ + $\text{H}_2$	0.50 0.35 0.15	$2.00 \times 10^{-10}$	$1.0^b (5.8 \times 10^{-10})^b$
$\text{C}_2\text{H}_3^+$	+ $\text{C}_2\text{H}_4$	$\text{C}_2\text{H}_5^+$ + $\text{C}_2\text{H}_2$	1.00	$6.90 \times 10^{-10}$	$1.0^c (8.9 \times 10^{-10})^d$
$\text{C}_2\text{H}_4^+$	+ $\text{C}_2\text{H}_4$	$\text{C}_3\text{H}_5^+$ + $\text{CH}_3$ $\text{C}_4\text{H}_7^+$ + $\text{H}$	0.90 0.10	$8.40 \times 10^{-10}$	$0.90^e \quad 0.91^f \quad 0.9^f (7.9 \times 10^{-10})^d$ $0.06 \quad 0.09 \quad 0.1$
$\text{CHCCNH}^+$	+ $\text{C}_2\text{H}_4$	$\text{H}_5\text{C}_5\text{N}^+$ + $\text{H}$		$<1.30 \times 10^{-9}$	
$\text{HC}_5\text{N}^+$	+ $\text{C}_2\text{H}_4$	$\text{H}_2\text{C}_5\text{N}^+$ + $\text{C}_2\text{H}_3$	0.75	$1.20 \times 10^{-9}$	

		H <sub>3</sub> C <sub>7</sub> N <sup>+</sup>	+ H <sub>2</sub>	0.05		
		H <sub>5</sub> C <sub>7</sub> N <sup>+</sup>		0.20		
HCNH <sup>+</sup>	+ C <sub>2</sub> H <sub>6</sub>	No Reaction			<2.0X 10 <sup>-11</sup>	
C <sub>3</sub> H <sub>6</sub> <sup>+</sup>	+ C <sub>3</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>7</sub> <sup>+</sup>	+ C <sub>3</sub> H <sub>5</sub>	0.15	1.40X10 <sup>-9</sup>	0.24 <sup>g</sup> (7.4 X 10 <sup>-10</sup> ) <sup>g</sup>
		C <sub>4</sub> H <sub>7</sub> <sup>+</sup>	+ C <sub>2</sub> H <sub>5</sub>	0.20		0.13
		C <sub>4</sub> H <sub>8</sub> <sup>+</sup>	+ C <sub>2</sub> H <sub>4</sub>	0.35		0.43
		C <sub>5</sub> H <sub>9</sub> <sup>+</sup>	+ CH <sub>3</sub>	0.30		0.20
Reactions with HCN						
C <sub>2</sub> H <sub>6</sub> <sup>+</sup>	+ HCN	HCNH <sup>+</sup>	+ C <sub>2</sub> H <sub>5</sub>	0.95	1.2 X10 <sup>-9</sup>	
		H <sub>6</sub> C <sub>3</sub> N <sup>+</sup>	+ H	0.05		
C <sub>3</sub> H <sub>5</sub> <sup>+</sup>	+ HCN	C <sub>3</sub> H <sub>5</sub> <sup>+</sup> .HCN	+ hv		-5.00X10 <sup>-**</sup>	
		Adduct				
C <sub>3</sub> H <sub>6</sub> <sup>+</sup>	+ HCN	Products			3.00x10 <sup>-10</sup>	
c-C <sub>3</sub> H <sub>6</sub> <sup>+</sup>	+ HCN	CH <sub>3</sub> CN <sup>+</sup>	+ C <sub>2</sub> H <sub>4</sub>	0.40	4.00x10 <sup>-10</sup>	
		H <sub>6</sub> C <sub>4</sub> N <sup>+</sup>	+ H	0.60		
C <sub>2</sub> N <sub>2</sub> <sup>+</sup>	+ HCN	Products			2.40x10 <sup>-9</sup>	HNC <sup>+</sup> + C <sub>2</sub> N <sub>2</sub> (0.20) <sup>h</sup> (2.7 x 10 <sup>-9</sup> ) <sup>h</sup> HC <sub>2</sub> N <sub>2</sub> <sup>+</sup> + CN(0.75) C <sub>2</sub> N <sub>2</sub> <sup>+</sup> .HCN (0.05)
						C <sub>3</sub> N <sub>3</sub> <sup>+</sup> + H (1.0) <sup>i</sup> (1.6 x 10 <sup>-11</sup> ) <sup>i</sup>
NO <sup>+</sup>	+ HCN	No Reaction			<8.00x10 <sup>-11</sup>	

Other Reactions				
$C_2H_2^+$	+ $N_2$	No Reaction		$<2.0 \times 10^{-11}$
$C_2H_5^+$	+ $N_2$	No Reaction		$<1.0 \times 10^{-11}$
$C_2H_2^+$	+ $C_2N_2$	No Reaction		$<2.0 \times 10^{-11}$
$C_2H_4^+$	+ $HC_3N$	$H_2C_3N^+$ $H_4C_5N^+$	+ $C_2H_3$ + $H$	$1.0^j (1.1 \times 10^{-9})$  no reaction <sup>k</sup>
$C_3H_5^+$	+ $H_2$	No Reaction		$<2.0 \times 10^{-11}$
$C_3H_5^+$	+ $HC_3N$	$H_2C_3N^+$ $C_3H_5^+ \cdot HC_3N$	+ $C_3H_4$	$\sim 1.00 \times 10^{-10}$ $<1.0 \times 10^{-23}$
$C_3H_5^+$	+ $CH_2CHCN$	$CH_2CHCNH^+$ $C_3H_5^+ \cdot CH_2CHCN$	+ $C_3H_4$	1.00

Footnote for Table 2

- <sup>a</sup> See ref. 30  
<sup>b</sup> See ref. 31  
<sup>c</sup> See ref. 32  
<sup>d</sup> See ref. 6  
<sup>e</sup> See ref. 33  
<sup>f</sup> See ref. 34  
<sup>g</sup> See ref. 35  
<sup>h</sup> See ref. 36  
<sup>i</sup> See ref. 37,38  
<sup>j</sup> See ref. 39  
<sup>k</sup> See ref. 40